Attachment A

Quality Assurance/Quality Control (QA/QC) Protocol

State of California

AIR RESOURCES BOARD

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROTOCOL

Detailed QA/QC Procedures for Air Monitoring of Certain Breakdown Products of Metam Sodium

Quality Management and Operation Support Branch

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C92-070

Report Date: October 15, 1992

Detailed QA/QC Procedures for Air Monitoring of
Certain Breakdown Products of Metam Sodium

I. Introduction

The Cal/EPA Office of Environmental Health Hazard Assessment (OEHHA) and the Department of Pesticide Regulation (DPR) have requested that the Air Resources Board (ARB) staff conduct ambient air monitoring for the primary breakdown product, methyl isothiocyanate (MITC), of metam sodium (sodium-N-methyldithiocarbamate). In response to this request, ARB staff will conduct a three-day source impacted ambient monitoring for MITC after an application of metam sodium, as well as an ambient monitoring program for MITC within populated areas.

Prior to the sampling program, the ARB staff, in cooperation with AIHL, will implement a quality assurance/quality control (QA/QC) program. The objective is to ensure the reliability and accuracy of the monitoring results. Based on the result of the QA/QC program, the existing sampling and analytical procedures may be modified to achieve the objective.

The compound of primary interest is MITC; however, attempts will be made to determine levels of hydrogen sulfide and carbon disulfide as well. Hydrogen sulfide will be measured by an on site direct reading portable analyzer. Carbon disulfide will be analyzed by ICI.

This protocol will be amended to reflect greater details in the QA/QC program as they become avaliable (Attachment A, Sections I and II).

II. Sampling

The ARB Engineering Evaluation Branch (EEB) staff will be responsible for the overall management of the monitoring program and for sample collection. EEB staff will calibrate all rotometers before use in the field. Prior to sample collection, a flow audit will be undertaken by the ARB Quality Management and Operations Support Branch (QMOSB) (see Attachment A, Section III). After sampling is completed, the EEB staff will check the calibration of the rotometers to ensure accurate measurements of the flow rates. The Jerome hydrogen sulfide analyzer will also be calibrated prior to use in the field.

Calibration and flow audits of the rotometers usually takes no more than one day. Therefore, changing the flow rate prior to sampling will not cause a significant delay.

III. Analysis

The QMOSB staff will conduct a system and a performance audit on AIHL. The system audit consists of responding to a questionnaire used to determine if the laboratory is implementing good laboratory practices. The performance audit (see Attachment A, Section IV for an example) consists of providing the laboratory with sample tubes containing various quantities of MITC (spike). The QMOSB will make triplicate spike tubes at each level. Two complete sets will be archived until the audit results are deemed acceptable. These

additional sets will be retrieved to resolve any discrepancy or address questions regarding MITC analysis (including spike preparations). AIHL will not know the MITC levels prior to analysis.

The standard to be used for spiking by QMOSB will be prepared from the neat (pure) compound provided by AIHL. AIHL will use this same standard for analysis (after appropriate dilutions). The procedure for the preparation of the spike was discussed between ARB and AIHL staff. AIHL believes the procedure to be appropriate.

The system and performance audits will take three to four weeks to complete. Therefore, if any breakdown products other than MITC (which require laboratory analysis as opposed to direct instrument readings) are desired, a delay of at least one month will be required to complete the laboratory audits. This is necessary to conduct certain studies to validate the analytical and sampling procedures. Validation is necessary to produce reliable and accurate results. If standards must be ordered or if other difficulties occur, the delay may be longer.

IV. Scheduling

Sampling for MITC is not anticipated before November, 1992. In order to start the MITC monitoring in November, the results of the QA/QC program must be available by late October. Completion of a QA/QC program in October will allow DPR and ARB to conduct monitoring in Imperial, Kern or Contra Costa County. Any unsatisfactory results from the audits will postpone the sampling until the difficulties are resolved.

Attachment A, Section I

Metam Sodium QA/QC Protocol Amendment, September 4, 1992

State of California

M E M O R A N D U M

To : Peter Ouchida
Manager,
Testing Section

Date : September 4, 1992

Subject : Metam Sodium QA/QC
Protocol Amendment

From : Don Fitzell
Air Resources Board

In order to further define the QA/QC procedure to be used prior to field sampling, a meeting was held September 2, 1992 among AIHL, ARB's QA Section and EEB. In addition to the system and performance audits to be conducted by the QA Section, two further studies were agreed to by all involved. First, AIHL would conduct desorption efficiency studies. Upon successful completion this would be followed by QA's system and performance audits. In addition, collection/conversion studies would be carried out by EEB (analysis by AIHL).

The desorption studies will consist of spiking 10 tubes at 3 different levels (0.1 ug, 0.5 ug and 2.0 ug) plus 2 blanks (thirty-two tubes, total). Five tubes at each level will be analyzed the following day to determine recovery levels. The remaining spikes will be analyzed after simulating the handling of the samples in the field (Stored in an ice chest for approximately one week prior to extraction).

The system and performance audits will be conducted as outlined in the protocol except only one set of spikes will be archived. Extra tubes will be spiked to be used in the collection/conversion studies. Four tubes at each of 4 levels (total of 16 tubes) will be prepared. This includes blanks. One set of duplicates at each level will be sent to AIHL for the performance audit and one set of duplicates will be archived. Duplicates (at two of the above levels plus blanks) will be prepared for the collection/conversion studies.

The collection/conversion study will consist of running ambient air through duplicate spike tubes (2 pairs) and duplicate blank tubes at two flow rates for 24 hours. The levels will be high enough above the limit of quantitation to insure detection. The two flow rates will be the same as anticipated for the study; 2 liters per minute and 4 liters per minute.

The desorption efficiency studies are anticipated to be completed around September 18. The performance audit spikes will be prepared and

the collection/conversion studies are expected to be conducted the week of September 21-25. This will allow the analyst time to complete his work prior to October 19.

If the above schedule can be followed, field sampling is expected to occur the first part of November in Kern County. The ambient monitoring (2 weeks) will be set up first and if possible, the application monitoring will be scheduled during the second week of the ambient monitoring.

Attachment A, Section II

MITC Application Meeting, Berkeley, October 1, 1992

State of California

M E M O R A N D U M

To : Interested Parties

Date : October 1, 1992

Subject : MITC Application Meeting, Berkeley

From : Don Fitzell
Air Resources Board

Yesterday at a meeting with AIHL and ARB's QA Section, the following items were agreed to as part of our QA program for the upcoming MITC application:

1. The flow rates for the collection/conversion study will be 1 and 4 liters per minute (lpm) rather than 2 and 4 lpm. The lower flow rate will be used for both the application and ambient monitoring IF the higher flow rate indicates breakthrough or a significant decrease in sensitivity. AIHL has demonstrated it can meet the required Minimum Detection Level (MDL) at this lower flow rate.

2. The performance audit tubes and the collection/conversion tubes will be spiked at levels between 0.2 - 3.0 ug per tube.

3. Back up (non-spiked) tubes will be used in series with the higher flow rate (4 lpm) collection/conversion spikes so that breakthrough can be confirmed, if present. These additional tubes do not need to be analyzed unless breakthrough is indicated.

4. By Wednesday morning, October 7, all of the QA tubes will be delivered to AIHL for analysis. There will be a total of 26 tubes, identified only by a number from 1 through 26. The tubes will have been spiked at 1 of 4 levels: 1) blank, 2) low, 3) medium and 4) high. The breakdown will be as follows:

Performance	Collection/conversion (battery)	Collection/conversion (AC)
	1 lpm	4 lpm
2 blank	2 blank	2 blank
2 low		
2 medium	2 medium	2 medium
2 high	2 high	2 high
		4 back up (for above)
8	6	10 TOTAL = 24

All of the above tubes will be prepared by ARB's QA Section. In addition, 3 more sets (1 blank, 1 low, 1 medium and 1 high) will be prepared. One set will go to DPR (or CDFA lab) for comparative studies and 2 sets will be archived (total 12 tubes). QA will prepare a total of 36 spiked tubes.

If there are any corrections, additions or comments, please call me at: (916) 445-0618 (ATSS 8-485-0618) or PES (DLF).

Attachment A, Section III

Flow Audit Procedure for Pesticide Samplers

Flow Audit Procedure for Pesticide Samplers

Introduction

The pesticide sampler is audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable Brooks automatic flow calibrator.

The audit device is placed in series with the sample probe inlet and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the pesticide sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fitting.
6. 1/4" I.D. Tygon tubing.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the teflon tubing to the outlet port of the audit device with the Swagelock fitting.
3. Connect the free end of the teflon tubing to the sampler probe inlet with a small section of Tygon tubing.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

Attachement A, Section IV

Performance Audit Procedure

Performance Audit Procedure
For The Laboratory Analysis Of Garlon and 2,4-D

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Garlon and 2,4-D. The audit is conducted by submitting audit samples prepared by spiking adsorbant tubes with known concentrations of Garlon and 2,4-D. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Garlon, 44.3% acid equivalent
2. 2,4-D, 41.9% acid equivalent
3. Methanol, pesticide analysis grade
4. XAD-2 Adsorbant Tubes
5. 50 ul Microsyringe

Safety Precautions

Garlon may cause irritation to skin, eyes, and mucous membranes. 2,4-D may cause cancer, cardiovascular system injury or liver damage, seizures, nausea, vomitting, airway obstruction, increased mucous secretions in the lungs, gastrointestinal disturbances and may be fatal if swallowed. Avoid direct physical contact. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Standards Preparation

4 mg/ml Garlon (acid equivalent) Stock Solution: Weigh about 90 mg of the Garlon formulation into a clean 10 ml volumetric flask and dilute with methanol to the mark. Record the concentration.

4 mg/ml 2,4-D (acid equivalent) Stock Solution: Weight about 95 mg of the 2,4-D formulation into a clean 10 ml volumetric flask and dilute with methanol to the mark. Record the concentration.

20 ug/ml Garlon (acid equivalent) Spiking Standard: Transfer 50 ul of the 4 mg/ml Garlon stock solution to a clean 10 ml volumetric flask and dilute with methanol to the mark. Record the concentration.

40 ug/ml 2,4-D (acid equivalent) Spiking Standard: Transfer 100 ul of the 4 mg/ml 2,4-D stock solution to a clean 10 ml volumetric flask and dilute with methanol to the mark. Record the concentration.

Sample Preparation

Prepare five audit samples from the 20 ug/ml Garlon and 40 ug/ml 2,4-D spiking standards according to the following table:

Sample	20 ug/ml Garlon Std Volume (ul)	40 ug/ml 2,4-D Std Volume (ul)
1	20	20
2	10	0
3	0	10
4	40	10
5	10	40

1. Break off the inlet end of the sample tube.

2. Insert the syringe needle into the adsorbant bed of the primary section of the tube, and slowly inject the appropriate volume of each spiking solution. Do not allow the liquid to run down the sides of the tube.

3. Cap the open end of the tube with the plastic cap provided.

4. Assign a random number to each sample, keeping track of the concentrations. Label each tube with its assigned number and store in a freezer until ready for analysis.

Attachment B

DPR's "Monitoring Recommendation for Metam-sodium"

State of California

Memorandum

To Genevieve A. Shiroma, Chief
Toxic Air Contaminant Identification Branch
Air Resources Board
1219 K Street, P.O. Box 2815
Sacramento, California 95812

Date : September 8, 1992

Place :

From Department of Pesticide Regulation - 1220 N Street, P.O. Box 942871
Sacramento, California 95814

Subject Monitoring Recommendation for Metam-sodium

On May 19,1992, Dr. Richard J. Jackson of the Office of Environmental Health Hazard Assessment (OEHHA), requested the Air Resources Board (ARB) and the Department of Pesticide Regulation (DPR) to document airborne emissions of methyl isothiocyanate (MITC), the degradation product and active fumigation component of the pesticide metam-sodium. This memorandum provides background and recent use information of products which contain metam-sodium, and identifies how these products are used.

Background

Technical metam-sodium [CAS # 137-42-8], and metam-sodium dihydrate [CAS # 6734-80-1] are colorless crystals with molecular weights of 129.18 grams/mole, and 165.21 g/mole respectively. Metam-sodium is soluble in water to 722 g/liter at 20 °C and has a negligible vapor pressure. The acute LD_{50} via oral administration is 280 mg/kg for mice and 820 mg/kg for rats. Acute oral LD_{50} for rats of MITC is 95 mg/kg. Metam-sodium is stable in concentrated aqueous solutions, but unstable in dilute aqueous solutions. Decomposition to MITC is promoted by acidic soils and heavy-metal salts. Metam-sodium has entered the risk assessment process at DPR under SB 950 (Birth Defect Prevention Act of 1984).

Metam-sodium is a pre-plant soil fumigant/sterilant used in California for the control of nematodes, soil borne fungi, and insects. Metam-sodium is a class 2 (moderately toxic) pesticide and is not a restricted material under section 6400, Title 3, California Code of Regulations. Prior to 1990, Pesticide Use Reports were not required for this chemical. Therefore, information for this recommendation is based solely on the 1990 Pesticide Use Report database.

In 1990, 5,934,082 lbs of metam-sodium active ingredient (AI) were reported to have been used to fumigate fields which were then planted out to various crops. A breakdown of metam-sodium use, and the crops which were then planted are shown in Table 1.

Table 1: Metam-sodium use in California in 1990.

Commodity	lbs. AI	lbs/Acre
Carrots	1,243,160	128.3
Tomato	951,998	45.1
Cotton	484,266	42.1
Potato	322,985	162.7
Cole crops	208,455	54.4
Melons	157,600	97.9
Onion	105,617	140.3
Fallow fields[a]	1,622,390	46.2
Other fumigations	837,638	--

a. Crops to be planted following fumigation were not specified.

Soil Fumigation

Information from the 1990 Pesticide Use Report indicates that a majority of metam-sodium use is for the fumigation of agricultural soils. Labels for metam-sodium containing products recommend application rates of 60-320 lbs AI per acre for broadcast or strip applications, via injection, or by chemigation. The higher use rates are recommended when soils are high in organic matter, or control of pests deep in the soil strata. For spot applications (soil treatment following removal of infested or diseased trees or grape vines), recommended application rates are 0.8 to 1.6 lbs AI per 100 square feet.

Monitoring Recommendation

Based on 1990 Pesticide Use Report data (Table 2), we recommend that the ARB monitor for MITC during September or October in Kern or Imperial County following a preplant metam-sodium application to carrots. Although applications continue throughout late fall and winter, sampling is not recommended at this time due to cooler weather and decreased volatility of metam-sodium and MITC.

Table 2: Metam-sodium use for Fresno, Imperial, and Kern Counties for September-December 1990

County	lbs AI	Acres
Fresno		
November	78,591	1,818
December	256,185	6,174

County	lbs AI	Acres
Imperial		
September	150,262	1,419
October	203,415	1,373
Kern		
September	12,250	51
October	108,428	698
November	106,811	639
December	179,359	1,269

DPR has recently issued a Section 18 emergency registration (#92-18) to allow methyl bromide (MeBr) to be used for soil sterilization. This Section 18 allows use of MeBr on 30,000 acres statewide for control of nematodes in soils to be planted to carrots for the period of July 17, 1992 through July 8, 1993. Use of MeBr under this Section 18 emergency registration may greatly reduce metam-sodium applications to soils to be planed to carrots.

We recommend that ARB contact the Kern or Imperial County Agricultural Commissioner for specific application times and locations. If you wish, DPR can assist in contacting the County Agricultural Commissioners for locating possible application sites.

If you have comments or questions, please contact Kevin Kelley, of my staff, at 654-0819.

John Sanders

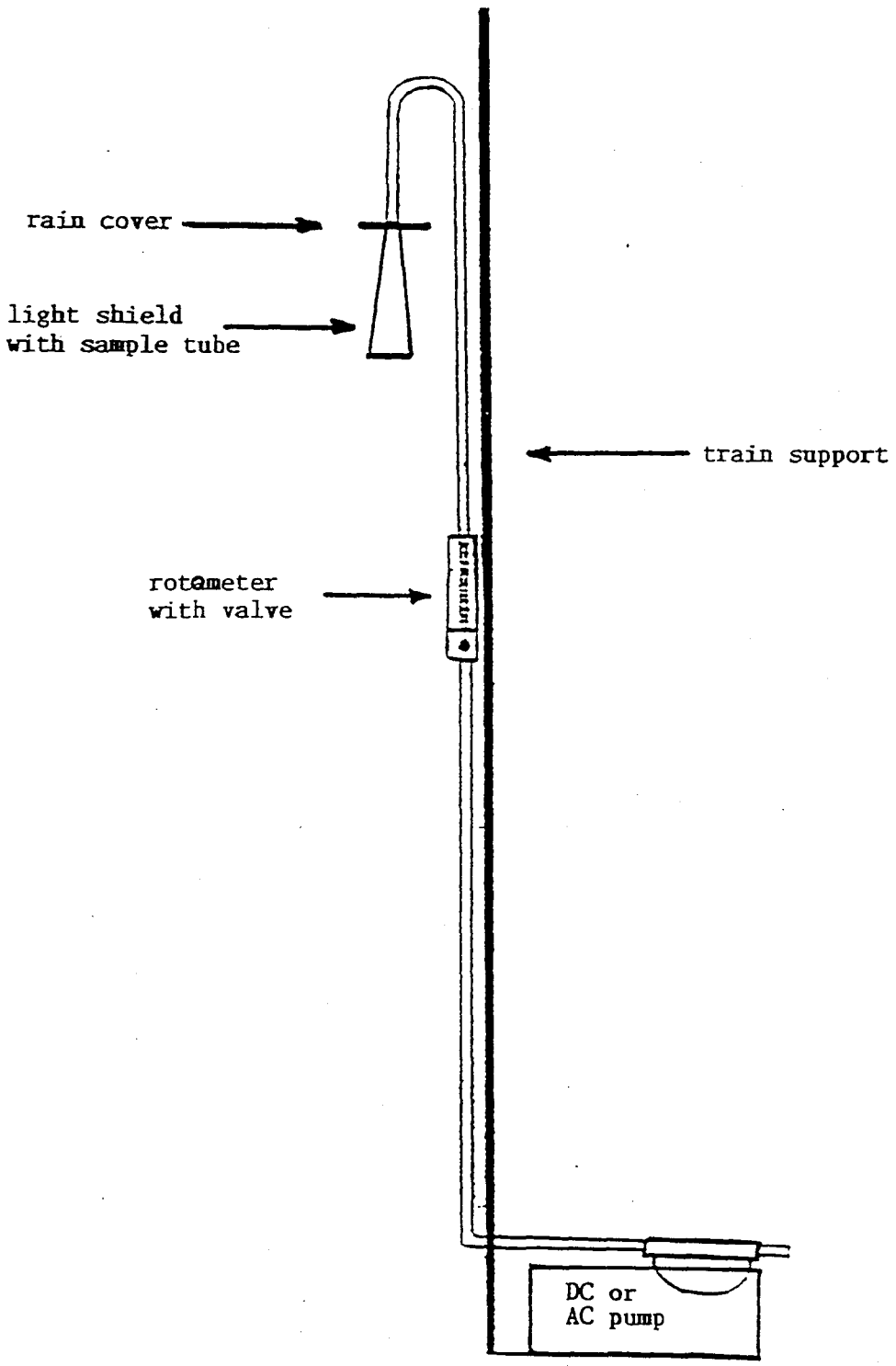
John Sanders
Acting Branch Chief
Environmental Monitoring and
Pest Management, Room A-149
(916) 654-1141

cc: Jim Wells
Ron Oshima
Lynn Baker
Kevin Kelley
Bill Lockett
Ted Davis
Mark Pepple
Joy Wisniewski
Jim Stratton
Mike DiBartolomeis
Richard Jackson
Stephen Birdsall

Attachment C

Pesticide Monitoring Apparatus

PESTICIDE MONITORING APPARATUS



Attachment D

ARB's "Quality Assurance Plan for Pesticide Monitoring"

State of California
Air Resources Board

Quality Assurance Plan for Pesticide Monitoring

Prepared by the

Monitoring and Laboratory Division
and
Stationary Source Division

September 28, 1990

APPROVED:

Veronica A Shum, Chief,
Toxic Air Contaminant
Identification Branch
Stationary Source Division

_____, Chief,
Quality Management and
Operations Support Branch
Monitoring and Laboratory Division

George Lew, Chief,
Engineering Evaluation Branch
Monitoring and Laboratory Division

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

LIST OF TABLES

APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Food and Agriculture (DFA), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. Short-term (one month) ambient monitoring will be conducted in the area of, and during the season of, peak pesticide applications. In addition, monitoring of a field during and after application (up to 72 hours) will occur. The purpose of this document is to specify quality assurance activities for sampling and laboratory analysis of the pesticide.

II. Quality Assurance Policy Statement

It is the policy of the ARB to provide DFA with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

III. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: 1) to establish the necessary quality control activities relating to site selection, sample collection, sample analysis, and data validation, and 2) assessment of data quality in terms of precision, accuracy and completeness.

IV. Siting

Siting criteria for ambient pesticide monitoring are listed in TABLE 1. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. Background sites should be located away from any applications.

Siting criteria for placement of samplers near a pesticide application for collection of short-term samples are: 1) fifteen yards upwind of the field, 2) fifteen yards downwind of the field, and 3) 150 yards downwind of the field. These are only guidelines, since conditions at the site will dictate the placement of monitoring stations. Data on wind speed and direction will be collected during application monitoring. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed. Field application monitoring will follow the schedule outlined in TABLE 2. This schedule and study design are consistent with requests from DFA for monitoring near a pesticide application.

A. Monitoring Site Description

The protocol for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations. A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions).

Similarly, a map or sketch of the monitoring stations should be made with respect to the application field.

V. Sampling

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Sampling will be conducted following the Environmental Protection Agency (EPA) ambient monitoring guidelines of 40 CFR 58 for calibration, precision, accuracy and data validation. The ARB Quality Assurance Section upon request will review quality assurance/quality control procedures and will evaluate pesticide monitoring activities.

A. Protocol

Prior to conducting any pesticide monitoring a protocol will be written that describes the overall monitoring program and includes the following topics:

1. Identification of the sample site locations.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.)

3. Description of the analytical method.

4. Quality assurance/quality control plan for sampling, including calibration procedures for flow meters.

5. Test schedule.

6. Test personnel.

Specific sampling methods and activities will be described in a monitoring plan (protocol) for review by ARB and DFA. Criteria which apply to all sampling are: 1) chain of custody forms will accompany all samples (APPENDIX I.), 2) light and rain shielding will be used for samples during monitoring and, 3) samples will be stored in an ice chest until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to this specific pesticide.

B. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample type (e.g., charcoal tube), sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results. Field blanks should be included with each batch of samples submitted to the lab for analysis. The average of the initial and final flow rates for the sampling period will be used if a flow controller is not used.

C. Collocation

For ambient monitoring, sampling precision or the standard deviation of the data set will be calculated from at least 2 samples collocated at a site. The collocated sampler will be rotated between sampling sites so that at least three duplicate samples are collected at each site. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. One sample will be designated as the primary sample and the other sample will be designated as the duplicate.

D. Calibration

If elapsed time meters are used, rather than noting beginning and ending times, the meters should be checked and calibrated to within $\pm$ 5 minutes for a 24-hour period. Samplers operated with an automatic on/off timer should be calibrated so that the sampling period is 24 hours $\pm$ 15 minutes.

Flow meters, flow controllers or critical orifices should be calibrated against a referenced flow meter prior to a monitoring period.

Sampling flows should be checked in the field and noted before and after each sampling period. Before flows are checked, the sampling system should be leak checked. The initial flow should be within $\pm$ 10% if a calibrated pressure transducer is used to check the flows, or within $\pm$ 15% if a calibrated rotameter is used. Flow meters should be recalibrated if flows are found to be outside of those control limits.

E. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc. should be made by sampling personnel.

TABLE 1. PESTICIDE MONITOR SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. APPLICATION SAMPLING SCHEDULE

The sampling schedule for each station is as follows:

	Samples per Site*		
	~15 yds up-wind	~15 yds down-wind	~150 yds down-wind
- Background sample (1 hr. sample: prior to application).	2	2	2
- Application + 1 hr. after application combined sample.	2	2	2
- 2 hr. sample from 1 to 3 hours after the application.	2	2	2
- 4 hr. sample from 3 to 7 hours after the application.	2	2	2
- 8 + hr. sample from 7 to 15+ hours after the application.	2	2	2
- 9 + hr. sample from 15 to 24+ hours after the application.	2	2	2
- 1st 24 hour sample starting at the end of the 9+ hr. sample.	2	2	-
- 2nd 24 hour sample starting 24 hrs after the end of the 9+ hr. sample.	2	2	-

* duplicate collocated samples at each site.

VI. Analysis

Analytical audits should be conducted by spiking the sample medium with the reference standard. These can then be carried into the field and handled as actual samples (trip spike) or run at the background site for ambient monitoring (field spike) prior to delivery to the laboratory for analysis. At least one spike per monitoring period is required and one spike per week is recommended for ambient monitoring.

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. should include: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures.

A. Standard Operating Procedures

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The monitoring plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable gas standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Assurance

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection. Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as; use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of lab analysis and after every tenth sample. Control samples should be found to be within control

limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked tubes at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VII. Data Reduction and Reporting

The mass of pesticide (microgram, ug) found in each sample will be used along with the sample air volume from the field data sheet to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in ug/m^3 as well as ppb or ppt (as appropriate). Wind speed and direction data will also be reported for application site monitoring.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum detection limit), total number of samples and number of samples above the minimum detection limit. For this purpose, collocated samples are averaged and treated as a single sample.

A. Quality Assurance

Quality assurance activities and data will be summarized by the staff conducting the sampling and included as an attachment to the final data summary. The quality assurance report will include a summary of the average data precision, accuracy, and completeness.

1. Precision and Accuracy

The average precision or standard deviation will be reported based on the comparison of the collocated sampling data. Accuracy data to be reported includes the results of the analyses of spiked samples and the results of any flow audits.

2. Data Completeness

Data completeness should be calculated as a percentage of valid data compared to the total possible amount of data if no invalidations had occurred. Data will be invalidated if the power is out at a site and the length of a sample time cannot be verified, or if any of the sampling medium is lost during sampling, shipment or analysis.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: __/__/_____
Sample/Run #: _____ Time: _____
Job name: _____
Sample Location: _____
Type of Sample: _____
Log #: _____

ACTION	DATE	TIME	INITALS	
Sample Collected				
			GIVEN BY	TAKEN BY
Transfer				
Transfer				
Transfer for Analysis				

ID #	LOG #	DESCRIPTION

RETURN THIS FORM TO: _____

Attachment E

AIHL Procedure for the Analysis of MITC

STATE OF CALIFORNIA—HEALTH AND WELFARE AGENCY PETE WILSON, Governor

DEPARTMENT OF HEALTH SERVICES
2151 BERKELEY WAY
BERKELEY, CA 94704-1011

(510) 540-3003

December 20, 1991

Mr. George Lew
Monitoring and Laboratories Division
Air Resources Board
P.O.Box 2815
Sacramento 95812

Dear Mr. Lew,

As part of the Dansmuir spill investigation, a number of XAD-2 and charcoal tubes were used to sample airborne methyl isothiocyanate (MITC). The samples were subsequently brought to AIHL/HML for analysis. The principal of the analytical methodology was based on the general NIOSH approach for volatile organic compounds that includes desorption with a suitable solvent and analysis by Gas Chromatography (GC) with an appropriate detector. In particular, the charcoal tubes were analysed for MITC by a method developed by ICI (Stauffer), with the minor modification of adjusting the extraction volume to accommodate the larger tube size.

In brief, each charcoal tube provided a front and a back section that was analysed separately. Each section was extracted with 2 mL of CS_2. The extracts were injected into a GC with a Nitrogen/Phosphorus detector (NPD). A 75 m DB 624 column was used under a temperature program of 4 min at 40° C, followed by 5° C/min to 120° C. The quantitation limit was 400 ng per section.

Each XAD tube provided a front and a back section that were analysed separately. Each section was extracted with 2 mL ethyl acetate. The extracts were analysed by GC with a Flame Photometric Detector (FPD). A 15 m DB 17 column was used at 80° C. The quantitation limit was 400 ng per section.

George Lew,

December 20, 1991

Our Laboratory Reports are on file. Please contact me if you need additional information.

Happy Holidays.

Sincerely,

Myrto Petreas, Ph.D., M.P.H.
Environmental Biochemist
Hazardous Materials Laboratory

cc: HML MITC File
M.Imada, AIHL
M.Fracchia, AIHL
S.Twiss, AIHL

Attachment F

ICI Procedure for the Analysis Of MITC

METHYL ISOTHIOCYANATE FROM METHAM-SODIUM

DETERMINATION IN AIR

Written by: S. C. Leung

Distribution List

1 - D. J. Brookman
1 - G. L. Cooper
1 - J. A. Kieft
1 - M. G. Kleinschmidt
1 - S. C. Leung
20 - J. C. McKay
1 - W. J. Smith
1 - WRC Central File

de Guigne Technical Center
August 26, 1982
Method No. RRC-82-35

NOTICE

This report is the property of, and embodies proprietary information belonging to, Stauffer Chemical Company. It must not be copied in whole or in part, nor the information shown therein disclosed to third parties except with the express written permission of Stauffer Chemical Company.

TITLE:

METHYL ISOTHIOCYANATE FROM METHAM-SODIUM
DETERMINATION IN AIR

I. SCOPE

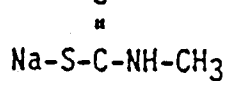
This method is designed to measure methyl isothiocyanate (MITC) in air. The method is applicable for methyl isothiocyanate concentrations between 0.01 and 6 mg per cubic meter in a 40-liter air sample. Methyl isothiocyanate is the active fumigant to which VAPAM® is converted upon application to soil.

II. SUMMARY OF METHOD

A known volume of air is drawn through a charcoal tube via a battery-operated sampling pump. The methyl isothiocyanate present in the air is quantitatively adsorbed on the charcoal. The charcoal is then desorbed with carbon disulfide; the extract is analyzed for methyl isothiocyanate by gas chromatography with nitrogen-phosphorus alkali flame ionization detection.

III. INTRODUCTION

VAPAM® soil fumigant, common name Metham-sodium, is sodium N-methyldithiocarbamate:



VAPAM® is generally formulated as an aqueous solution containing 32.7% anhydrous sodium salt and is nonvolatile. Its activity is due to decomposition to methyl isothiocyanate (CH_3NCS).

IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5710A or equivalent, equipped with a nitrogen-phosphorus alkali flame ionization detector (NP-AFID).

2. Recorder. Sensitivity of 1 millivolt full scale, 1 second response.

3. Quantitation Aid. Electronic digital integrator, on-line data acquisition system or other device for measuring peak areas.

4. Gas Purification Traps. For purifying helium, air and hydrogen required for gas chromatograph. Model 236 (Guild Corp., P. O. Box 217, Bethel Park, PA 15102) or equivalent.

5. Gas Chromatograph Column. Pyrex tubing (1.8 m x 2 mm i.d.), washed with KOH solution, silanized and dried. Pack the tubing with 10% SP 2250 on 100/120 mesh Supelcoport or equivalent. See Appendix A for details of column preparation and conditioning.

6. Syringe. 10-microliter capacity with fixed needle, Hamilton 701N or equivalent.

7. Personal Air Sampling Pump. DuPont P-200 or equivalent; capable of drawing 100 mL/minute of air through the charcoal tube for 8 hours.

8. Glass Vials. 2-dram, equipped with polyseal-lined caps.

9. Charcoal Tubes. Glass tube with both ends flame sealed, 7 cm long with a 6-mm o.d. and a 4-mm i.d., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. Such charcoal tubes are commercially available from SKC, Inc., Eighty four, PA 15330, Cat. No. 226-01.

10. Charcoal Tube Holder. Nylon sample tube holder equipped with collar clip and tygon connecting tube for supporting the charcoal tube in a vertical position in the employee's breathing zone. SKC Cat. No. 222-3-1, or equivalent.

11. Silica Gel Tubes. For use as moisture pre-trap in the presence of high (>80%) relative humidity. These are glass tubes with both ends flame sealed, 7 cm long with a 6-mm O.D., containing 2 sections of 75/150 mg of silica gel. SKC Cat. No. 226-10, or equivalent.

B. Reagents

1. Carbon Disulfide. Mallinckrodt AR grade, Cat. No. 4352 or equivalent.

2. Gases. Supplied to gas chromatograph via lines equipped with gas purification traps and suitable line regulators.

   a. Helium. High purity cylinder helium.

   b. Hydrogen. High purity cylinder hydrogen.

   c. Air. Dry air, free from organic contaminants, from cylinder or compressor.

3. Methyl Isothiocyanate. Analytical Reagent grade. Aldrich Cat. No. 11777-1.

IV. PROCEDURE

A. Air Sampling

Break both ends of the charcoal tube to provide openings for air to pass through. The smaller section of charcoal is used as a backup section and therefore is placed nearest the sampling pump. Use tubing from the sample tube holder to connect the back of the tube to the pump. Turn on the pump and set the flow rate to 100 mL/min. Calibrate the trap-pump assembly via RRC method 76-46; record the calibration data.

To take an air sample, support the charcoal tube in a vertical position with the sample tube holder and clip the trap to the employee's clothing so that the trap is located as close as possible to his or her breathing zone. Attach the pump to the employee via a convenient pocket. Turn on the pump, and take a 6-8 hour sample. At the end of the sampling period record the time. Remove the trap-pump assembly from the employee; recalibrate the assembly and record the recalibration data.

For sampling at relative humidity greater than 80%, connect a silica gel tube in front of the charcoal tube by means of a short tygon tubing during the entire sampling period. The silica gel is used as a drying agent preceding the charcoal to eliminate the effect of moisture (see Section VI.B.).

B. Gas Chromatographic Conditions

Set the temperature of oven, injection port, and detector on the gas chromatograph. Establish suitable flow rates for the various gases; optimizing the detector response according to the manufacturer's directions.

The following conditions are given for a Hewlett-Packard Model 5710A chromatograph with a N-P AFID detector and a 1.8 m x 2 mm i.d., 10% SP2250 column.

Column temperature:	95°C, isothermal
Injection port temperature:	250°C
Detector temperature:	300°C
Helium carrier gas flow:	30 mL/min
Hydrogen flow:	3 mL/min
Air flow:	60 mL/min
Quantitation:	digital integrator or data system; set attenuation to obtain a measurable peak from 0.5 ng of MITC.

Under the above conditions, MITC elutes in approximately 2.4 minutes.

C. Calibration

Prepare five calibration standards containing 0.1, 1.0, 5.0, 10.0 and 20.0 micrograms of methyl isothiocyanate per mL of carbon disulfide to cover the desired range of calibration. Prepare standard solutions fresh weekly, and refrigerate standard solutions when not in use. Inject 5.0 microliters of each solution into the chromatograph at least twice and record the peak areas. Plot the average peak area against the corresponding MITC concentration (micrograms/mL), and draw the best-fitted straight line through the points. Check calibration periodically by occasionally alternating injections of standards with those of samples.

D. Sample Analysis

Score each charcoal tube with a file in front of the glass wool plug and break the tube open. Remove the glass wool plug and place it in a 2-dram vial that contains 1.0 mL of carbon disulfide. Pour the charcoal in the front section into the vial, tapping the side of the tube to dislodge any charcoal that adheres to the walls. Immediately cap the vial with a polyseal-lined cap. Remove the separating foam plug

and transfer the backup section into another 2-dram vial containing 1.0 mL of carbon disulfide; immediately cap the vial. Desorb the MITC for 30 minutes, agitating the sample occasionally to facilitate desorption.

Inject 5.0 microliters of the carbon disulfide extract from each section of the charcoal tube into the gas chromatograph. Dilute the extract if necessary to keep the response(s) within the range. Analyze the sample extracts immediately after calibration has been completed. If analysis of the extract cannot be completed on the same day, refrigerate the extract at 0°C. However, do not store the extract for more than 2 days due to the high volatility of carbon disulfide.

V. CALCULATIONS

A. Mean Flow Rate

Calculate the mean flow rate for the pump-trap assembly by the following equation:

$$F = \text{mean flow rate (L/min)} = \frac{A + B}{2}$$

where A = average initial flow rate, L/min
B = average final flow rate, L/min

B. MITC Concentration in Air

Use the calibration curve and the MITC peak area obtained from the sample extract to determine the amount of MITC in each section of the trap. Calculate the concentration of MITC in air by the following equation:

$$\text{MITC concentration } (mg/M^3) = \frac{(W1 + W2)}{F \times T}$$

where W1 = weight of MITC found in front section of charcoal tube, micrograms

W2 = weight of MITC found in backup section of charcoal tube, micrograms

F = mean flow rate, L/min
T = sampling time, minutes

VI. DISCUSSION

A. Precision and Accuracy

Desorption Efficiency (DE) for MITC was determined by introduction of known amounts of MITC directly into charcoal tubes at levels of 0.5, 5, 25, and 50 micrograms of MITC. Six replicates were prepared at each of the above levels. All samples were analyzed; the D.E. of MITC is shown in Table 1 (see Reference B for statistical procedure used).

The collection efficiency of this method was tested by generating MITC vapors with the use of the dynamic U-tube system adapted from the literature (References C & D). An average MITC recovery of 94% was obtained for 26 test trials with a relative standard deviation of 10%. Recovery data for MITC in air are shown in Table 2.

The present method was applied also to aqueous solutions of metham-sodium. In this recovery test, a known amount of metham-sodium in aqueous solution was injected onto moistened vermiculite placed at one end of the U-tube while air was pulled through the U-tube at 0.1 L/min and carried the MITC vapors into a charcoal tube at the other end of the U-tube. The presence of water and vermiculite is known to speed up the rate of decomposition of metham-sodium to MITC (Reference E). At the end of each sampling test, both sections of each charcoal tube were removed for desorption and analysis to obtain recovery of MITC. Under these conditions, at least 75% of metham-sodium (up to 190 ug) was converted to MITC in 5 hours. Longer time (16 hours) was required for the conversion of 380 ug of metham-sodium. A summary of the recovery data of MITC from metham-sodium in air is shown in Table 4.

B. Other Comments

The effect of humidity on the recoveries of MITC from air was also studied. A summary of recovery data from air of various relative humidities (R.H.) is shown in Table 5. No significant losses occurred when MITC was sampled at R.H. between 50% and 70%. However, at lower concentrations (less than 0.01 mg/M^3) and R.H. greater than 80%, humidity has a more serious effect (see Table 5). To avoid losses of MITC due to effects of moisture, the use of a silica gel tube preceding the charcoal tube is recommended for sampling at R.H. greater than 80%. Recoveries of MITC at high R.H. (>81%) with the use of the silica gel pre-trap showed no significant differences from recoveries at lower R.H. (see Table 6).

Experimentally no breakthrough was observed when 230 micrograms of MITC was adsorbed in the charcoal tube from air with 70 liters of air pulled through the tube at a sampling flow rate of 200 mL/min. This was determined by analysis of both the front and the backup section of the charcoal tube. In general, if more than 25% of the total sample is in the backup section, significant breakthrough may have occurred and the sample is not valid.

Storage stability tests indicated that recoveries of samples stored for 14 days under refrigeration at 4°C agreed within ±15% relative to those of initial samples (see Table 2).

VII. SAFETY PRECAUTIONS

A. Methyl Isothiocyanate

Methyl isothiocyanate is toxic, skin irritant and lachrymator.

Avoid contact with skin and eye.

Avoid inhalation of mist, sprays or vapors.

Use only with adequate ventilation and wear gloves.

B. Carbon Disulfide

Carbon disulfide is flammable and vapor harmful.

Keep away from heat and open flame.

Keep container closed.

Use only with adequate ventilation.

Avoid prolonged breathing of vapor.

Avoid prolonged or repeated contact with skin.

VIII. REFERENCES

A. WRC Notebook: 7397-34 to 50
7411-9 to 36
7550-25 to 44
7893-7 to 10

B. D. G. Taylor, R. E. Kupel, and J. M. Bryant, "Documentation of the NIOSH Validation Tests", DHEW (NIOSH) Publication No. 77-185, 1977.

C. L. W. Severs, R. G. Melcher and M. J. Kocsis, Am. Ind. Hyg. Assoc. J., 39, 321 (1978).

D. R. G. Melcher, R. R. Langer and R. O. Kagel, Am. Ind. Hyg. Assoc. J., 39, 349 (1978).

E. R. A. Gray and H. G. Strein, Phytopathology, 52, 734 (1962).

Written by: S. C. Leung /xx
S. C. Leung
Senior Research Chemist

Approved by: M. G. Kleinschmidt
M. G. Kleinschmidt
Supervisor, Analytical Section

Approved by: D. J. Brookman
D. J. Brookman
Manager, Analytical Section

Appendix A

A. Column Preparation and Conditioning

Wash inside of Pyrex column with 1% aqueous KOH and let stand filled with KOH solution 15 minutes. Rinse well with four successive methanol and two successive toluene washes. Fill column with a solution of 5% dimethyldichlorosilane in toluene and let stand 15 minutes. Drain and rinse with toluene. Finally, rinse with methanol and dry with a stream of nitrogen.

Pack the gas chromatographic column with the 10% SP 2250 packing under moderate vacuum with light tapping. Do not use a vibrator. The packing should not extend into the end areas of the column that are heated by the injection port and detector. Install the packed column in the chromatograph with the exit end free. Turn on the carrier gas to 20-40 mL/min, set the initial temperature to 80°C and hold it there for about 30 minutes. This will purge the column of oxygen and water vapor. Increase the column temperature at a rate of 2°C/min. The final conditioning temperature should be 240°C. Condition the column eight hours or more with 20-40 mL/min of carrier gas flowing. After conditioning, cool the oven and complete the installation of the column.

Table 1. Desorption Efficiency (D.E.) of Methyl Isothiocyanate

Test 1			Test 2			Test 3			Test 4		
µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.
0.50	0.42	0.84	5.14	4.71	0.92	21.4	19.8	0.93	51.5	52.3	1.02
0.50	0.43	0.86	5.14	4.93	0.96	21.4	20.1	0.94	51.5	53.0	1.03
0.50	0.43	0.86	5.14	4.86	0.95	21.4	19.8	0.93	51.5	51.4	0.99
0.50	0.43	0.86	5.00	4.60	0.92	21.4	20.4	0.95	51.5	50.6	0.98
n =		4			4			4			n
Mean D.E. =		0.86			0.94			0.94			1.01
St. dev. =		0.010			0.021			0.0096			0.024
CV_1 =		0.012			0.022			0.010			0.024

$$\overline{CV}_1 = 0.018$$

NOTES: CV_1 = coefficient of variation

$\overline{CV}_1$ = Pooled coefficient of variation.

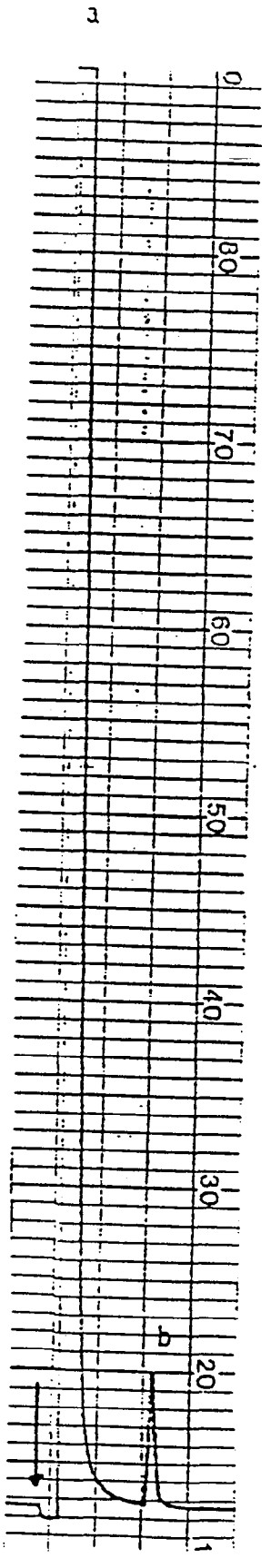
Table 2. Storage Stability of Methyl Isothiocyanate

Test 1			Test 2			Test 3			Test 4		
µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery
0.50	0.42[a]	84	5.14	4.71[a]	92	21.44	19.8[a]	92	51.45	52.3[a]	102
0.50	0.43[a]	86	5.14	4.93[a]	96	21.44	20.1[a]	94	51.45	53.0[a]	103
0.50	0.43[a]	86	5.14	4.86[a]	95	21.44	19.8[a]	92	51.45	51.1[a]	99
0.50	0.43[a]	86	5.00	4.60[a]	92	21.44	20.4[a]	95	51.45	50.6[a]	98
0.50	0.39[b]	78	5.15	5.16[b]	100	25.47	24.6[b]	97	51.45	50.1[b]	97
0.50	0.39[b]	78	5.15	5.19[b]	101	25.47	24.3[b]	95	51.45	45.3[b]	88
0.50	0.38[c]	76	5.15	4.59[c]	89	25.47	23.2[c]	91	51.45	46.8[c]	91
0.50	0.37[c]	74	5.15	4.71[c]	92	25.47	22.6[c]	89	51.45	55.6[c]	108
0.50	0.38[c]	76	5.14	4.11[c]	80	21.44	15.9[c]	74	51.45	44.9[c]	87
0.50	0.39[c]	78	5.14	4.01c	78	21.44	16.7[c]	78	51.45	45.7c	89

NOTES: a = Samples analyzed after being stored for 1 day under refrigeration
b = Samples analyzed after being stored for 7 days under refrigeration
c = Samples analyzed after being stored for 14 days under refrigeration
% Recovery not corrected for desorption efficiency (D.E.)

FIGURE 1. Typical Chromatogram for MITC Analysis

Standard, 1 ug/mL



a = Solvent

b = MITC, 2.3 min.

Sample 7397-49-8, at 5.1 ug MITC

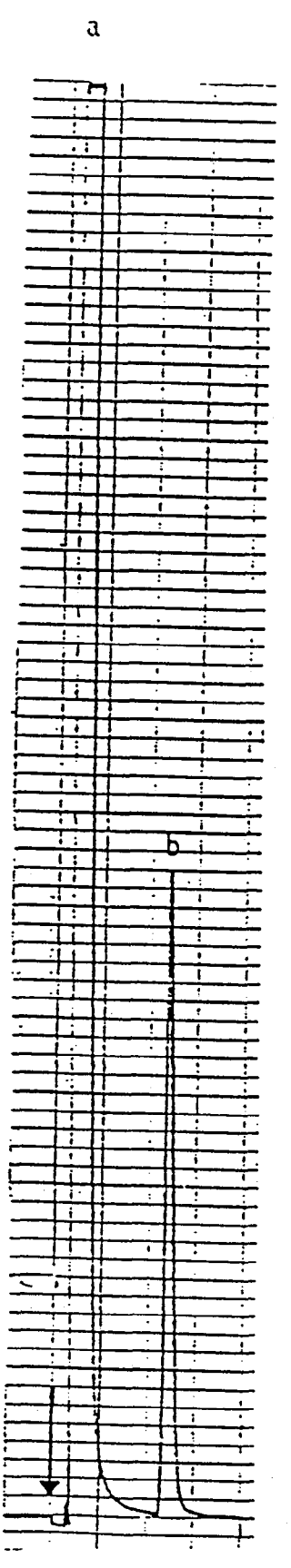


Table 3. Recovery Data for MITC in Air

Temperature = 65-68°F; R.H. = 58-70%

L/min Flow Rate	Minutes Sampling Time	Liters Air Volume	ug MITC Taken	ug MITC Found	% Recovery
0.1	430	48	0.5	0.44	88
0.1	430	40	0.5	0.44	88
0.1	430	45	0.5	0.44	88
0.1	510	47	0.5	0.36	72
0.1	510	52	0.5	0.37	74
0.1	510	53	0.5	0.39	78
0.1	410	40	5.15	4.20	82
0.1	410	40	5.15	4.49	87
0.1	410	43	5.15	4.72	92
0.1	380	36	5.15	4.71	92
0.1	420	39	5.15	5.34	104
0.1	430	44	5.15	5.05	98
0.1	420	40	10.29	10.9	106
0.1	460	43	25.47	27.3	107
0.1	460	47	25.47	25.7	101
0.1	460	45	25.47	26.0	102
0.1	450	50	25.47	25.3	99
0.1	450	42	25.47	25.2	99
0.1	450	48	25.47	24.2	95
0.1	360	38	51.45	46.9	91
0.1	370	37	51.45	48.6	94
0.1	450	45	51.45	48.5	94
0.1	450	46	51.45	53.4	104
0.1	460	46	51.45	49.5	96
0.1	390	38	51.45	50.6	98
0.1	450	47	227.4	207	91
0.2	370	71	227.4	195	86*
0.2	370	71	225.6	180	80*
0.2	370	66	225.6	179	79*

Mean = 94
RSD = 10%
n = 26

NOTES: % Recovery not corrected for desorption efficiency (D.E.)

* = Samples collected at flow rates greater than 0.1 L/min; not included in the calculation of mean % recovery

SAMPLE PREPARATION:

5. Detach and discard drying tube. Place front and back sorbent sections of sampler tube in separate vials. Discard glass wool and foam plugs.
6. Pipet 1.0 mL toluene into each vial. Cap each vial.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to toluene in 10-mL volumetric flasks and dilute to the mark to prepare solutions in the range 0.02 to 0.5 mg CS_2/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph ([peak area]$^{1/2}$ vs. mg CS_2).
   NOTE: The FPD has a small linear range. Additional working standards may be required.
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (1 to 20 µL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg CS_2 recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1600-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: The retention time for toluene is ca. 30 min, which may be shortened by temperature programming.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of desorbed sample with toluene, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass (corrected for DE), mg, of CS_2 found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of CS_2 in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:
This method modifies S248, in that 1 mL toluene (instead of 10 mL benzene) is used to desorb samples, resulting in a better desorption efficiency at low levels and safer working conditions for the analyst [8]. Method S248 [5] was issued on January 30, 1976, and validated over the range 15 to 59 mg/m³ using a 6-L sample with spiked samplers and atmospheres generated by syringe pump/triple air dilution and verified by total hydrocarbon analyzer [2]. Overall precision, S_r, was 0.059 with "found" concentrations 0.8% lower than "true" concentrations for 18 samples tested, representing a non-significant bias. Breakthrough (with drying tube preceding charcoal tube) occurred at 162 min (100% RH, 40 ppm CS_2, 0.2 L/min sampling rate) = 32.4 L; DE (0.28 to 1.12 mg/sample) = 0.86; storage stability (0.56 mg/sample) = 85% recovery after one week at 25 °C. At a 1 L/min sampling rate, breakthrough occurred at 19 L at 100 mg/m³ [4]. A user check of this method gave an estimated LOD of 0.02 mg CS_2 per sample [3].

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Carbon Disulfide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-156 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] Documentation of the NIOSH Validation Tests, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[3] User check, UBTL, Inc., NIOSH Sequence #3990-L (unpublished, November 9, 1983).
[4] McCammon, C. S., P. M. Quinn and R. Kupel. A Charcoal Sampling Method and a Gas Chromatographic Analytical Procedure for Carbon Disulfide, Am. Ind. Hyg. Assoc. J., 36, 618-624 (1975).
[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[6] Ibid., Vol. 1, PSCAM 179; U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[7] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123, available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[8] Foley, G. D. NIOSH/OPSE (internal memo, April 17, 1985).

METHOD REVISED BY: Mary Lynn Woebkenberg, NIOSH/OPSE; S248 originally validated under NIOSH Contract CDC-99-74-45.

PROTOCOL AMENDMENT

Study: EF-91-360

Title: METAM-SODIUM APPLICATOR EXPOSURE

PART I. Field Protocol
PART II. Analytical Phase

Amendment: 3. (Analytical Phase)

Study Director: Thomas J. Meyers

Date: 19 Dec 91

Copy to: Study File (Original)
Diana Graham
Bill Ja (QA)
Kim Tufts (Morse Labs)
Aaron Rotandaro (Pan-Ag. Labs)

Details: The is being written in response to conversations with the EPA on 16 and 17 December 1991. Additional dynamic validations of air sampling methodology has been agreed.

The validation data must conform to Subdivision U. The validations will be conducted at WRC.

1) Validation data for MITC at 1.0 L/min flow rate and 400 mg charcoal tube.

a) Subdivision U states: "The extraction efficiency of laboratory fortified controls will be considered acceptable if the lower limit of the 95 percent interval is greater than 70 percent, unless otherwise specified by the Agency. At a minimum seven determinations at each fortification level to calculate the mean and standard deviation for recovery. Total recovery from field fortified samples must be above 50 percent for the study."

2) Validation data for MITC at 0.5 L/min flow rate.

a) same as above using 100 mg charcoal tube.

3) Validation data for CS2 at 0.5 L/min flow rate.

a) same as above using 400 mg charcoal tube.

Reference standards of MITC (ASW 1275 C) and CS2 (ASW 1419) will be used to prepared fortification and calibration solutions.

Fortifications for MITC will be prepared as outlined below:

FORTIFICATION PROCEDURES - MITC

Solvent	Acetone

Solutions	Amount	Level
100,000 mg/L	7.0 µL	700 µg
100 mg/L	10.0 µL	1.0 µg

Syringe	10 microliter (µL)
Matrix	Charcoal tubes 100/50 and 400/200 mg

FORTIFICATION PROCEDURES - CS2

Solvent	Acetone

Solutions	Amount	Level
1,000 mg/L	10.0 µL	100 µg
100 mg/L	10.0 µL	1.0 µg

Syringe	10 microliter (µL)
Matrix	Charcoal tubes 400/200 mg

Prepare a standard charcoal tube as for sampling by scoring and breaking both ends of the glass tube. Make sure the pump is running at correct flow rate. Fill the 10 microliter syringe with the appropriate amount of the fortification solution. Place the tip of the syringe needle into the glass wool of the front portion of charcoal. The needle should also be as centered as possible. After discharging the syringe, place caps on both ends of the tube.

MITC. Charcoal tubes will be analyzed for MITC using method RRC 82-35 "Methyl Isothiocyanate from Metam-sodium; Determination in Air." issued 26 August 1982. The method is to be modified for use of 0.1 % carbon disulfide in ethyl acetate as an extracting solvent instead of the listed solvent carbon disulfide. Method

will be modified for use of jumbo tubes, 400/200 mg charcoal tubes. The extraction volume of solvent will be 5.0 mL. See appendix B of analytical protocol for typical gas chromatographic conditions.

Carbon Disulfide. Charcoal tubes will be analyzed for carbon disulfide using NIOSH method 1600 "Carbon Disulfide" revision #1 issued 15 May 1985. The extracting solvent will be 5.0 mL of toluene cooled and saturated with dry ice.

GAS CHROMATOGRAPHY. Calibrate the gas chromatography using standards prepared from the reference standards as mentioned above. For the lower calibration limits, the 1 µg fortifications, use 0.1 and 0.2 mg/L calibration solutions. Higher fortifications can be determined using standards and diluting the extracts to within a linear range of the detector and standards. Peak heights may be used for quantitation.

As part of each set which may consist of one or more GC runs, include a solvent spike, two method desorption samples (tube fortifications with dynamic flows), a charcoal blank, and seven determinations.

Thomas Meyers 30 Dec 91

Thomas Meyers, Study Director Date

PROTOCOL AMENDMENT

Study: EF-91-360

Title: METAM-SODIUM APPLICATOR EXPOSURE

PART I. Field Protocol
PART II. Analytical Phase

Amendment: Field Protocol and Analytical Phase

Study Director: Thomas J. Meyers

Date: 29 Jan 92

Copy to: Study File (Original)
Diana Graham
Bill Ja (QA)
Kim Tufts (Morse Labs)
Aaron Rotandaro (Pan-Ag. Labs)
Ameesha Metha (EPA, fax 212 264-6119)
Curt Lunchick (EPA, fax 703 305-5147)

Details: The is being written in response to a conversation held with the CREB on 27 January 1992. The following changes in the previously agreed protocol (signed by study director on 01 Nov 91) will be as follows:

1 Flow rates

For collection of MITC (Methyl Isothiocyanate) vapors in the field, the flow rate will be calibrated at 1.0 L/min using charcoal tubes of 400/200 mg, "jumbo" tubes.

For collection of CS2 (Carbon Disulfide) vapors in the field, the flow rate will be calibrated at 0.5 L/min using charcoal tubes of 400/200 mg, "jumbo" tubes.

2 Pilot program

A pilot program for field validation of sampling methodologies will be initiated before the application scheduled for Arizona at the end of February.

3 Number of Replicates at Arizona Site

At the Arizona site two applications will be conducted. One application will be sprinkler (overhead set); the other application will be soil injection using a shank. This second application using a shank is a change in the current protocol, page 6, that has specified this application would use a rotary tiller. Rotary tiller will be still planned for use later at the Washington site. See below.

a) Sprinkler (Chemigation) have 10 replicates.

b) Soil injection will use shank (with multi injectors) and have 10 replicates. Two replicates will use open cab; 6 replicates will use closed cabs without carbon filtration; 2 replicates will use closed cabs with commercially available carbon filtration.

4 Number of Replicates at Washington Site

At the Washington site two applications will be conducted. One application will be sprinkler (center pivot); the other application will be soil injection using a rotary tiller as currently specified.

a) Sprinkler (center pivot) will have 5 replicates.

b) Soil injection (rotary tiller) will have 10 replicates.

5 Downwind Sampling

Page 8 of the field protocol is amended for sampling at four locations from the downwind edge of the application zone: 0 m, 25 m, 50 m, and 100 m (m=meter). Any significant change in the wind direction will necessitate that the sampling location will be moved to correspond to the new downwind direction.

6 Field-Fortifications Samples

a) Controls will be run simultaneously with the field fortified samples. The location for each set of field fortifications will be selected to avoid any off site drift.

b) In the procedure for field fortifications, the syringe needle should be placed onto the front of the glass wool plug, instead of the center of the front portion of charcoal as had been previously specified.

7 Method modifications - MITC

The part II of the protocol, the analytical phase, is being amended for the use of 400/200 mg charcoal tubes instead of the 100/50 tubes as currently specified. The method RRC 82-35 should be modified as follows:

Use 5.0 mL of 0.1 % carbon disulfide in ethyl acetate to extract front or back segments of charcoal in each 400/100 mg tube. Maintain the same limit of quantitation for each tube, i.e., 1 ug per tube segment. For limits of quantitation use a gas chromatographic calibration standard of 0.2 ug/mL or less of MITC in 0.1 % CS2 in ethyl acetate.

8 Method modifications - CS2

The part II of the protocol, the analytical phase, is being amended for the use of 400/200 mg charcoal tubes instead of the 100/50 tubes as currently specified. The NIOSH method 1600 should be modified as follows:

Use 5.0 mL of toluene to extract front or back segments of charcoal in each 400/100 mg tube. The toluene must be prechilled using solid carbon dioxide. Carbon dioxide is necessary to increase the recovery at low fortification levels of carbon disulfide. Use a minimum of 2 grams of solid carbon dioxide. The outside of the glass vessel should be well cooled and frosted. Add charcoal from either tube segment while the toluene is still cooled but no solid carbon dioxide is remaining. Remove extracts from the glass extraction vessels before three hours but not before a minimum of one hour of extraction. Maintain the same limit of quantitation for each tube, i.e., 1 ug per tube segment. For limits of quantitation use a gas chromatographic calibration standard of 0.2 or less ug/mL of CS2 in toluene.

9 Analytical Validation Data

The analytical validation which was submitted in mid-Jan 1992 is to be included in the final report.

Thomas A. Meyers 30 Jan 92

Thomas Meyers, Study Director Date

Table 4. Recovery Data for MITC from Metham-sodium in Air

L/min Flow Rate	Minute Sampling Time	Liters Air Volume	ug Metham-Sodium Taken	Theoretical ug MITC Taken	ug MITC Found	% MITC Found based on Theoretical MITC Taken
0.11	380	42	23.7	13.4	11.9	89
0.12	400	50	47.0	26.8	25.4	95
0.12	320	38	94.7	53.5	46.3	87
0.12	320	40	189.5	107.2	84.1	79
0.12	430	52	189.5	107.2	79.3	74
0.11	990	110	189.5	107.2	78.7	73
0.11	320	36	379.0	214.0	110	51*
0.11	440	48	379.0	214.0	99	46*
0.13	990	125	379.0	214.0	190	89

NOTES: * = low recoveries on these samples due to incomplete conversion of MITC from Metham-sodium.

Table 5. Effects of Relative Humidity (R.H.) on Recoveries of MITC from Air

Sampling Flow Rate = 0.1 L/min.

% R.H.	No. of Samples	Hours Sampling Time	Liters Air Volume	ug MITC Taken	% Recovery
58	3	7	40 - 48	0.5	88* (87 - 88)**
70	3	7	47 - 53	0.5	74 (71 - 79)
81	4	7	38 - 44	0.5	43 (32 - 57)
81	2	4	25	0.5	66 (59 - 72)
92	3	7	41 - 42	0.5	53 (41 - 63)
92	2	4	22 - 25	0.5	72 (70 - 75)
58	3	7	36 - 44	5	98 (92 - 104)
70	3	7	40 - 43	5	87 (82 - 92)
81	5	7	34 - 57	5	50 (44 - 58)
81	2	4	21 - 24	5	69 (66 - 72)
92	3	7	37 - 42	5	55 (48 - 62)
92	3	4	20 - 26	5	83 (78 - 89)
58	3	7	43 - 47	25.5	103 (101 - 107)
70	3	7	42 - 49	25.5	98 (91 - 99)
81	1	6	35	25.5	78
92	3	7	39 - 41	25.5	77 (73 - 82)
92	1	4	26	25.5	76
58	2	6	37 - 38	51.5	93 (91 - 94)
70	4	7	38 - 46	51.5	98 (94 - 104)
81	1	6	36	51.5	97
81	1	6	39	227.4	80
92	1	6	36	51.5	100
92	1	7	42	102.9	100
92	1	7	41	227.4	83

NOTES: * = Mean
** = Range
% Recovery not corrected for desorption efficiency (D.E.)

Table 6. Recovery Data for MITC in Air at High (>81%) Relative Humidity with the Use of Silica Gel as a Pre-trap for Moisture

Sampling Flow Rate = 0.1 L/min.

% R.H.	Hours Sampling Time	Liters Air Volume	ug MITC Taken	ug MITC Found	% Recovery
81	6	36	0.5	0.40	79
81	7	42	0.5	0.37	74
81	7	41	5	4.43	89
81	7	46	5	4.35	87
92	6	38	0.5	0.38	75
92	7	45	0.5	0.36	71
92	7	44	5	4.39	88
92	7	44	5	4.21	84
92	7	46	25	22.9	92
92	7	45	25	22.7	91
92	7	46	59	55.9	95
92	7	40	59	51.9	88

NOTE: % Recovery not corrected for desorption efficiency (D.E.)

Attachment G

ICI Procedure for the Analysis of Carbon Disulfide

CARBON DISULFIDE

FORMULA: S=C=S; CS_2

M.W.: 76.14

METHOD: 1600
ISSUED: 2/15/85
REVISION #1: 5/15/85

OSHA: 20 ppm; C 30 ppm; P 100 ppm
NIOSH: 1 ppm; 10 ppm/15 min [1]
ACGIH: 10 ppm (skin)
(1 ppm = 3.11 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.263 g/mL @ 20 °C;
BP 46.5 °C; MP -112 °C;
VP 40 kPa (300 mm Hg; 40% v/v) @ 20 °C;
explosive range 1 to 50% v/v in air

SYNONYMS: dithiocarbonic anhydride; CAS #75-15-0.

SAMPLING

SAMPLER: SOLID SORBENT TUBE + DRYING TUBE
(coconut shell charcoal, 100 mg/50 mg, and sodium sulfate, 270 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2 L @ 10 ppm
-MAX: 25 L

SHIPMENT: dryer attached to charcoal

SAMPLE STABILITY: 1 week @ 25 °C;
6 weeks @ 0 °C

FIELD BLANKS: 10% (≥2) of samples

ACCURACY

RANGE STUDIED: 46 to 183 mg/m³ [2]
(6-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.059 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, SULFUR FPD

ANALYTE: sulfur

DESORPTION: 1 mL toluene; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 145 °C
-COLUMN: 30 °C

CARRIER GAS: N_2 or He, 20 mL/min

COLUMN: glass, 2 m x 6 mm OD, 5% OV-17 on 80/100 mesh GasChrom Q or equivalent

CALIBRATION: standard solutions of CS_2 in toluene

RANGE: 0.05 to 0.5 mg per sample

ESTIMATED LOD: 0.02 mg per sample [3]

PRECISION (s_r): 0.052 @ 0.28 to 1.1 mg per sample [2]

APPLICABILITY: The working range is 10 to 200 mg/m³ (3 to 64 ppm) for a 5-L air sample and is applicable to ceiling determinations. Better sensitivity may be obtained by using higher sampling rates if high humidity is not present [1,4]. This method has been used extensively in the viscose rayon industry and at carbon disulfide production facilities.

INTERFERENCES: No interference occurs from hydrogen sulfide [4]. Water vapor is a potential sampling interferent [4] which is removed by the drying tube. Alternate GC columns, e.g., 5% OV-210 on Chromosorb G-HP, aid in resolution of chromatographic interferences.

OTHER METHODS: This revises Method S248 [5] and Method 1600 (dated 2/15/84). The criteria document method [1] uses a higher sampling rate. This method replaces P&CAM 179 which uses a similar collection method but extraction-atomic absorption for measurement [6].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Toluene, chromatographic quality.
3. Calibration stock solution, 0.0253 mg/μL. Dilute 0.253 g CS_2 (0.200 mL at 20 °C) to 10 mL with toluene. Prepare in duplicate.
4. Oxygen, purified.
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Drying tube: glass tube, 7 cm long, 6 mm OD, 4 mm ID; single 270-mg section of granular anhydrous sodium sulfate between two silylated glass wool plugs. This removes moisture equivalent to 6 L of air at 100% RH and 22 °C.
   b. Sorbent tube: glass tube, 7 cm long, 6 mm OD, with flame-sealed ends and plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Available commercially.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. PTFE tubing, 5-mm ID.
4. Refrigerant, bagged (0 °C).
5. Gas chromatograph, FPD with sulfur filter, integrator and column (see page 1600-1).
   NOTE: A valve to vent the solvent peak when it elutes from the column is useful to protect the detector.
6. Vials, glass, 25-mL, PTFE-lined caps.
7. Volumetric flasks, 10-mL.
8. Syringe, 10-μL, readable to 0.1 μL.
9. Delivery pipets, 1- to 100-μL and 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C) [1,7]; work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing. Connect the drying tube to the front section of the charcoal tube with a 20-mm section of PTFE tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 2 to 25 L.
   NOTE: Samples may be taken up to 1 L/min if ambient humidity is low [1,4].
4. Keep the drying tube connected to the charcoal tube during shipping. Refrigerate (0 °C) to prevent CS_2 migration to the back section. Cap the open ends. Pack securely for shipment.

APPENDIX II.

PCA RECOMMENDATION

Recommendation #
0074

PESTICIDE USE RECOMMENDATION

RONALD NUNN FARMS
741 SUNSET RD.
BRENTWOOD, CA 94513
PHONE: (510) 634-2148

DATE: 3/8/93
PROPOSED APP. DATE: 3/8/93
LOCATION: Wallace #95
S/Hwy. 4, .25 M W/ Sellers Ave.
CROP: Tomato Beds

PERMIT #: 07-93-070077B
ACRES: 95 ACTUAL TREATED: 95

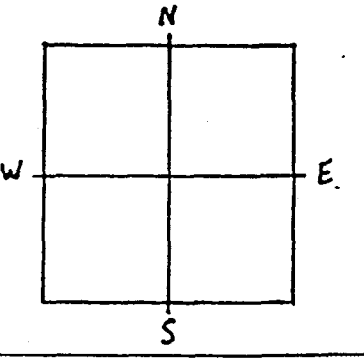
SECTION: 19 TOWNSHIP: 01 N RANGE: 03 E B+M: M

APPLICATOR: Grower METHOD OF APPLICATION: Ground VOLUME: 18 gal/Acre

	MATERIAL:	RESTR	EPA #	RATE:	/100 GALLONS	PEST:
1	Vapam	NO	10182-150	18 gal/A	Non/Dilute	fumigation
2						
3						
4						
5						
6						
7						

	YES	NO		YES	NO
NOI REQUIRED:		✓	TOXIC TO BEES		✓
POSTING REQ:	✓		TOXIC TO FISH	✓	
RE-ENTRY INTERVAL: 48 hours			TOXIC TO BIRD		✓
DAYS TO HARVEST: N/A					

PLANT BACK RESTRICTION: Do not plant within 14-21 days after Vapam application.



ALL ALTERNATIVE AND MITIGATION MEASURES HAVE BEEN CONSIDERED

DO NOT DRIFT

COMMENTS: Additional Information on back —

SIGNATURE: [signature] PCA #: 2747

Environmental Conditions

March 8, 1993

approx 12:15 p.m.

Temp. - 78 F

Humidity - Moderate

Clear skies, Winds from the E-SE 1-3 mph

Soil moisture - approx. - 70%

Target Pest - fumigation for suppression or control of:

1) Morning glory
   Nightshade
   Nutsedge

2) Disease Control of seedling disease
   Pythium - Damping off
   Phytophthora Root Rot

APPENDIX III.

CIMIS METEOROLOGICAL DATA

Hourly Weather Data for Station # 47 Brentwood — CIMIS Project

DATE	HOUR	ETo in.	PRECIP in.	RADIATION SOLAR --Ly/day--	RADIATION NET --Ly/day--	VAPOR PRESS mBars	AIR TEMP F	REL HUM %	DEW PNT F	WIND SPEED mph	WIND DIR 0-360	RSULT WIND mph	SOIL TEMP F
3/ 8/93	1	0.00	0.0	-5	-56	14.54	57.6	90	55	3.7	292	3.5	53
	2	0.00	0.0	-5	-56	14.48	56.9	92	54	2.0	309	1.7	53
	3	0.00	0.0	-5	-56	14.22	56.0	93	54	2.3	306	2.0	53
	4	0.00	0.0	-5	-56	13.75	55.0	93	53	1.7	321	1.7	53
	5	0.00	0.0	-5	-56	13.23	53.8	94	52	3.4	310	3.2	53
	6	0.00	0.0	-5	-56	12.57	52.3	94	51	2.1	185	0.3	53
	7	0.00	0.0	17	-44	12.04	50.9	95	49	2.6	120	0.4	53
	8	0.00	0.0	230	77	12.57	52.0	95	51	1.5	216	0.8	53
	9	0.01	0.0	670	328	14.04	55.3	94	54	2.3	214	1.5	53
	10	0.01	0.0	1085	589	15.36	59.3	89	56	2.2	235	1.2	53
	11	0.02	0.0	1439	792	16.03	63.7	79	57	2.5	143	1.1	53
	12	0.02	0.0	1652	950	16.19	66.8	72	58	3.1	103	1.5	53
	13	0.02	0.0	1687	975	16.53	69.4	67	58	3.0	110	1.3	53
	14	0.02	0.0	1605	911	16.57	71.6	63	58	4.1	109	2.8	54
	15	0.02	0.0	1169	663	16.10	73.0	58	57	3.8	111	2.4	54
	16	0.01	0.0	882	465	15.87	73.8	56	57	3.3	94	2.0	54
	17	0.01	0.0	562	255	16.47	73.8	58	58	3.1	199	1.9	54
	18	0.00	0.0	114	-5	15.86	71.2	61	57	5.3	317	4.6	55
	19	0.00	0.0	-2	-91	13.53	66.5	61	53	6.8	305	6.7	55
	20	0.00	0.0	-4	-92	12.31	63.8	61	50	4.4	296	4.3	55
	21	0.00	0.0	-4	-94	11.32	62.3	59	48	3.7	299	3.6	55
	22	0.00	0.0	-4	-92	11.39	60.0	65	48	3.5	302	3.4	55
	23	0.00	0.0	-4	-92	11.56	59.3	67	48	2.5	288	2.3	55
	24	0.00	0.0	-4	-90	11.68	57.7	72	49	4.3	312	4.2	55
3/ 8/93		0.12	= TOTAL ETo										
3/ 9/93	1	0.00	0.0	-5	-44	12.07	55.8	79	50	6.5	306	6.4	55
	2	0.00	0.0	-5	-43	12.30	54.8	84	50	5.9	299	5.8	55
	3	0.00	0.0	-5	-43	12.28	54.9	84	50	5.1	301	5.0	55
	4	0.00	0.0	-4	-43	12.18	54.3	85	50	3.8	319	3.6	55
	5	0.00	0.0	-5	-43	11.88	52.8	87	49	3.0	302	1.9	55
	6	0.00	0.0	-5	-43	11.88	52.0	90	49	2.9	332	0.2	54
	7	0.00	0.0	11	-35	11.93	51.7	91	49	2.9	193	0.8	54
	8	0.00	0.0	159	55	12.89	54.1	90	51	7.4	112	4.6	54
	9	0.00	0.0	361	159	13.23	55.9	87	52	4.4	302	3.3	54
	10	0.01	0.0	984	539	13.79	59.8	79	53	3.9	322	2.1	54
	11	0.02	0.0	1366	778	14.31	64.0	70	54	2.6	157	0.7	54
	12	0.01	0.0	1143	661	14.34	66.6	64	54	3.6	38	2.7	54
	13	0.02	0.0	1741	1012	14.65	69.0	60	55	3.4	338	1.3	54
	14	0.01	0.0	965	537	14.45	68.3	61	54	7.8	346	6.8	55
	15	0.00	0.0	352	109	14.10	66.9	63	54	6.1	12	5.7	55
	16	0.00	0.0	365	143	14.19	65.6	66	54	4.3	12	4.0	55
	17	0.00	0.0	365	153	14.01	65.4	66	54	5.5	341	5.3	55
	18	0.00	0.0	92	13	13.48	63.1	68	53	5.3	339	5.2	55
	19	0.00	0.0	-2	-54	13.55	60.3	76	53	5.3	319	5.2	55
	20	0.00	0.0	-4	-54	13.60	59.0	80	53	4.6	295	4.5	55
	21	0.00	0.0	-4	-54	13.20	57.7	81	52	2.9	279	2.6	55
	22	0.00	0.0	-5	-54	12.98	57.3	81	51	2.6	318	1.0	55
	23	0.00	0.0	-5	-54	12.76	56.0	83	51	3.4	83	2.2	55
	24	0.00	0.0	-5	-54	12.40	54.3	86	50	4.8	322	4.0	55
3/ 9/93		0.09	= TOTAL ETo										
3/10/93	1	0.00	0.0	-5	-97	11.80	53.0	86	49	3.1	359	1.6	55

Ly/day*.484=W/sq.m in.*25.4=mm (F-32)*5/9=C mph*.447=m/s mBars*.1=kPa

SEVERE FLAGS
N/A-not available N/C-not collected
S-not in service noc-cannot calculate
R-out of range I-ignore,no meaning

INFORMATIVE FLAGS
Y-out of range Q-all QC not done
F-estimated *PRELIMINARY DATA*
note: TOTAL ETo = sum of hourly ET

Hourly Weather Data for Station # 47 Brentwood — CIMIS Project

DATE	HOUR	ETo in.	PRECIP in.	RADIATION SOLAR Ly/day	RADIATION NET Ly/day	VAPOR PRESS mBars	AIR TEMP F	REL HUM %	DEW PNT F	WIND SPEED mph	WIND DIR 0-360	RSULT WIND mph	SOIL TEMP F
	2	0.00	0.0	-5	-97	11.25	50.4	90	48	2.8	176	1.2	55
	3	0.00	0.0	-5	-97	11.08	49.3	93	47	2.5	266	2.3	55
	4	0.00	0.0	-5	-96	11.45	50.0	93	48	3.1	240	2.6	55
	5	0.00	0.0	-5	-97	10.83	48.4	94	47	2.2	145	1.6	55
	6	0.00	0.0	-5	-97	10.45	47.3	94	46	1.9	229	0.6	54
	7	0.00	0.0	39	-68	10.21	46.5	95	45	2.1	312	0.9	54
	8	0.00	0.0	370	132	12.12	51.2	94	50	2.6	215	2.4	54
	9	0.01	0.0	810	342	13.76	57.8	84	53	3.5	54	3.1	54
	10	0.01	0.0	1187	606	14.71	62.7	76	55	2.8	337	0.3	54
	11	0.01	0.0	951	530	14.60	63.7	72	55	3.8	247	2.2	54
	12	0.01	0.0	710	338	14.34	64.3	70	54	4.0	293	3.0	54
	13	0.01	0.0	1016	573	14.28	65.6	66	54	4.5	284	3.2	54
	14	0.02	0.0	1211	707	14.08	66.0	65	54	8.0	292	7.5	54
	15	0.02	0.0	1305	728	14.06	67.0	62	54	8.7	307	8.2	55
	16	0.01	0.0	1016	527	13.78	67.0	61	53	10.0	300	9.7	55
	17	0.01	0.0	544	250	13.56	66.2	62	53	9.8	291	9.6	55
	18	0.00	0.0	184	37	13.67	64.0	67	53	9.1	296	8.9	55
	19	0.00	0.0	0	-82	13.05	60.8	72	52	6.8	276	6.6	55
	20	0.00	0.0	-5	-81	12.78	58.5	76	51	3.9	236	3.6	55
	21	0.00	0.0	-4	-81	12.56	56.4	81	51	4.0	298	3.0	55
	22	0.00	0.0	-5	-80	12.66	55.5	84	51	5.1	255	4.2	55
	23	0.00	0.0	-5	-80	12.36	54.3	86	50	3.0	214	2.7	55
	24	0.00	0.0	-5	-80	11.91	52.8	87	49	1.9	230	0.4	55
3/10/93		0.10	= TOTAL ETo										
3/11/93	1	0.00	0.0	-5	-87	11.74	51.5	90	49	1.8	234	1.2	55
	2	0.00	0.0	-5	-88	11.36	50.3	91	48	2.2	275	1.3	55
	3	0.00	0.0	-5	-88	11.06	49.3	93	47	1.3	208	0.2	54
	4	0.00	0.0	-5	-88	10.60	47.9	93	46	1.5	138	0.5	54
	5	0.00	0.0	-5	-88	10.43	47.3	94	46	3.0	177	2.8	54
	6	0.00	0.0	-5	-88	10.31	46.8	95	45	1.9	179	1.4	54
	7	0.00	0.0	37	-60	10.25	46.5	95	45	2.6	274	2.5	54
	8	0.00	0.0	361	135	12.96	53.1	94	51	7.5	294	7.3	54
	9	0.01	0.0	821	351	13.99	58.1	85	54	9.5	318	9.2	53
	10	0.01	0.0	1225	631	13.04	61.5	70	52	8.6	328	8.3	53
	11	0.02	0.0	1543	865	13.08	63.3	66	52	7.9	354	7.4	53
	12	0.02	0.0	1724	1002	13.63	65.6	64	53	6.2	319	5.2	54
	13	0.02	0.0	1778	1040	13.71	68.5	58	53	5.3	341	4.5	54
	14	0.02	0.0	1677	961	13.37	70.0	53	52	5.6	356	4.4	54
	15	0.02	0.0	1424	771	13.48	71.1	52	53	4.9	4	4.1	54
	16	0.01	0.0	1050	495	13.17	72.0	49	52	4.3	301	2.8	54
	17	0.01	0.0	605	276	12.87	71.8	48	51	4.7	280	4.2	55
	18	0.00	0.0	176	13	12.95	70.3	51	51	4.2	317	3.6	55
	19	0.00	0.0	0	-97	13.93	65.4	65	53	3.1	321	3.0	55
	20	0.00	0.0	-4	-94	14.34	61.6	77	54	3.0	261	2.6	55
	21	0.00	0.0	-4	-93	13.98	59.6	80	54	3.3	234	3.0	55
	22	0.00	0.0	-4	-93	13.59	58.2	82	53	3.2	239	2.9	55
	23	0.00	0.0	-5	-94	12.79	56.7	81	51	2.4	227	1.7	55
	24	0.00	0.0	-5	-93	12.29	53.7	87	50	2.3	149	1.9	55
3/11/93		0.13	= TOTAL ETo										

Ly/day*.484=W/sq.m in.*25.4=mm (F-32)*5/9=C mph*.447=m/s mBars*.1=kPa

SEVERE FLAGS

N/A-not available N/C-not collected
S-not in service noc-cannot calculate
R-out of range I-ignore,no meaning

INFORMATIVE FLAGS

Y-out of range Q-all QC not done
F-estimated *PRELIMINARY DATA*
note: TOTAL ETo = sum of hourly ET

APPENDIX IV.

JEROME CALIBRATION DATA

STATE OF CALIFORNIA — DEPARTMENT OF WATER RESOURCES — THE RESOURCES AGENCY

COMPUTATION SHEET

10/29/92

	TIME:	Conc. H_2S ppb (Actual)	Jerome 621 Display ppb	
1	0951	116	107	
2	0951		107	
3	0952		108	
4	0953		109	107.8
5	1004	57	55	
6	1006		56	
7	1006		54	
8	1007		55	55.0
9	1014	9.9	08	
10	1014		08	
11	1015		09	
12	1015		08	8.3
13	1018	ZERO	~~00~~	
14	1019		01	
15	1020		~~0~~	
16	1020		~~0~~	.2

$Y = 1.0637X - 0.0136$ $r = .2227$

CONC = 1.063 (READING) − 0.013

PERFORMED BY LJJ

MINIMUM DETECTION LIMIT = 3 PPBV

APPENDIX V.

PRE-TEST QA/QC RESULTS

State of California

M E M O R A N D U M

To : Peter Ouchida, Manager
Testing Section

Date : December 7, 1992

Subject : Summary of C92-070
MITC QA/QC Results

From : Don Fitzell
Assoc. Air Pollution Spec.
Air Resources Board

The performance audits prepared by ARB's QMOSB for AIHL and the CDFA laboratory (under contract to DPR) prior to an application monitoring revealed unexpected data (Attachment I). The most obvious is the greater than 100% recovery for both laboratories. In addition, AIHL apparently found significant amounts of MITC in the blank collection/conversion (c/c) samples (samples 9, 11, 16 and 18, Attachment I). I commented on the problem with the false positives found in the blanks (Attachment II).

AIHL conducted further studies to resolve these discrepancies. They analyzed four more audit samples (samples 28, 29, 30 and 31) which had been archived at the time of the first audit (see Attachment III). They also compared their standard solutions to that prepared by QMOSB and used to spike the audit samples for both AIHL and CDFA. The results (Attachment III, page 4) indicated the standard used by QMOSB to be 40% higher than that used by AIHL and CDFA [This is assuming that: 1) The recovery levels by both labs are unrealisticly high - 144% and 126% - and 2) it is more likely that one lab - QMOSB - made a dilution error rather than two]. All of the spiked levels in Attachment III have been changed to reflect this higher value. The percent recovery, based on these new numbers (Attachment III, page 1), are more realistic and in line with ICI's stability studies (Attachment IV).

To resolve the question of the false positives in the c/c samples, additional blanks were run in Sacramento and sent to AIHL for analysis. Also, the extracts from samples 9, 11, 16, and 18 were sent to the CDFA Sacramento Laboratory for analysis (Attachment V). No MITC peak was observed on the chromatograms of the additional c/c samples taken in Sacramento. CDFA laboratory confirmed the presence of an apparent MITC peak in the extracts for samples 9, 11, 16 and 18 provided by AIHL.

These data indicate that the original c/c samples analyzed by AIHL contained an interferent which for unknown reasons were not duplicated in subsequent samples. In order to minimize the

possibility of this occurring in the field samples, AIHL has recommended that EEB take background (blank) samples in the area targeted for monitoring a week prior to the actual monitoring. If feasible, I feel this is strongly advisable.

I believe the questions arising from the performance audit have been addressed. Whenever a field application of metam sodium can be arranged, AIHL is ready to perform the analysis.

cc: George Lew
Lynn Baker
Ruth Tomlin
Gabe Ruiz
Mike Poore
Miles Imada
Nancy Miller
Jeff Cook

Attachment 1

QA/QC Audit Results

Sample ID	Spike Level	Detected (ug)	Percent Recovered	Corrected for Blank (ug)		Percent Recovered
		DPR Performance Audit				
22	2.50	2.84	114			114
23	0.50	0.58	116			116
24	1.00	1.25	125			125
25	1.00	1.07	107			107
26	2.50	2.69	108			108
27	0.50	0.56	112			112
21	Blank	ND	--		AVG.	114
		AIHL Performance Audit				
1	2.500	3.489	140			140
3	0.500	0.629	126			126
4	1.000	1.198	120			120
5	2.500	3.002	120			120
7	1.000	1.375	138			138
8	0.500	0.547	109			109
2	Blank	ND	--		AVG.	126
6	Blank	ND	--			
		AIHL Collection/Conversion 1 liter/min.				
10	1.000	1.167	117	1.009		101
12	2.500	1.977	79	1.819		73
13	2.500	1.981	79	1.823		73
14	1.000	1.142	114	0.984		98
9	Blank	0.169			AVG.	86
11	Blank	0.148				
		AIHL Collection/Conversion 4 liter/min.				
15	2.500	3.224	129	2.698		108
17	1.000	1.462	146	0.936		94
19	1.000	1.505	150	0.979		98
20	2.500	3.144	126	2.618		105
16	Blank	0.557			AVG.	101
18	Blank	0.496				

Attachment II

State of California

M E M O R A N D U M

To : Miles Imada
Supervising Air Pollution
Research Specialist

Date : November 10, 1992

Subject : MITC Interferences

Through: Peter Ouchida, Manager
Testing Section

Don Fitzell
Assoc. Air Pollution Spec.

From : Air Resources Board

After our phone conversation of November 5, I am summarizing the data already known, postulating reasonable causes and suggesting possible avenues of approach to resolve this question.

To summarize the information we have at this point:

1. No MITC was detected in the blank performance audit samples analyzed by either your group or DPR.

2. Apparent MITC was detected by your laboratory in the blank collection/conversion (c/c) samples provided by our group. These charcoal tubes were spiked by the ARB Quality Management and Operation Support Branch. Air was drawn through these tubes at the Monitoring and Laboratory Division Shop at two flow rates (1 and 4 liters per minute) over a 24-hour period. The amount detected was proportional to the volume of ambient air drawn through the tubes.

3. Subsequent GC/MS analysis by your staff indicated the apparent MITC detected in the c/c blanks was not MITC.

4. Most of the samples received from the Dunsmuir spill last year indicated no MITC present. Recovery studies conducted by DPR did not indicate any interferences with MITC.

We must resolve the question of this interference detected in the c/c blanks before we attempt field sampling. At this point, I see three possibilities:

1. The interferences detected are common environmental compounds which can be readily detected anywhere and which can be separated from MITC by altering the chromatography program.

2. The interferences were environmental compounds specific to the air around the MLD Shop (vehicle exhaust, solvents, etc.) and would not be picked up in an actual field sampling.

3. The interferences were a one time occurrence (unique ambient air conditions at the time of sampling, accidental sample contamination, etc.) that cannot be reproduced or determined.

A number of experiments are possible to help to explain the results so far:

1. An analysis of the additional c/c blanks prepared by the MLD Shop (during the rainy period last week).

2. If any remaining extract containing the contaminant is left, analyze the remaining samples using the NPD with a chromatographic program similar to that used by ICI for the Dunsmuir spill samples, or that used by DPR for its analysis.

3. We are asking DPR to provide background samples from their application monitoring this week. The samples will be taken prior to application.

4. A review of the chromatograms from the c/c samples at the time of the Dunsmuir spill may help.

These are possible starting points to determine what may be causing the interference your staff detected in the c/c blanks. I'm sure your staff has other ideas as well. If we can be of any help in resolving this question, feel free to call me.

cc: George Lew

Attachment III

MITC QA/QC AUDIT RESULTS

DPR PERFORMANCE AUDIT

SAMPLE #	MITC Spiked Level (µg) QA VALUE	MITC Spiked Level (µg) AIHL CORRECTED VALUE	Detected (µg)	% Recovery†
22	2.5	3.5	2.84	81
26	2.5	3.5	2.69	77
24	1.0	1.4	1.25	89
25	1.0	1.4	1.07	76
23	.5	0.7	0.58	83
27	.5	0.7	0.56	80
21		Blank	ND	
Overall				80

AIHL PERFORMNANCE AUDIT (Analyzed Oct 14-20, 1992)

1	3.5	3.005	86
5	3.5	2.589	74
4	1.4	1.133	81
7	1.4	1.195	85
3	0.7	0.556	79
8	0.7	0.489	70
2	Blank	ND	
6	Blank	ND	
Overall			80

2nd AIHL PERFORMANCE AUDIT (Analyzed Nov 3, 1992)

31	3.5	1.894	54
30	1.4	0.732	52
29	0.7	0.412	56
28	Blank	ND	
Overall			54

AIHL ND = <0.025 µg/mL or <0.075 µg/sample

†For each group, overall recovery is calculated as the sum of the MITC detected, divided by the sum of the MITC spike, times 100.

MITC COLLECTION/CONVERSION EFFICIENCY RESULTS

1 L/min

SAMPLE #	MITC Spiked Level (µg)	Detected (µg)	% Recovery† (Corr. for Blank)
12	3.5	1.968	52
13	3.5	1.905	50
10	1.4	1.048	64
14	1.4	1.138	71
9	Blank	0.163 } mean	
11	Blank	0.131 } 0.147	
Overall			56

4 L/min

15	3.5	3.040	73
20	3.5	2.720	64
17	1.4	1.394	66
19	1.4	1.328	61
16	Blank	0.495 } mean	
18	Blank	0.442 } 0.468	
Overall			67

†For each group, overall recovery is calculated as the sum of the MITC detected, divided by the sum of the MITC spike, times 100.

MITC SPIKE AND PURGE/BREAKTHROUGH RESULTS

1 L/min

SAMPLE #	SPIKE (µg)	MITC DETECTED (µg) Front	Back	Total	% Breakthru
12	3.5	1.735	0.233	1.968	12
13	3.5	1.905	ND	1.905	0
10	1.4	0.834	0.214	1.048	20
14	1.4	1.138	ND	1.138	0
9	Blank	0.163	ND	0.163	0
11	Blank	0.131	ND	0.131	0

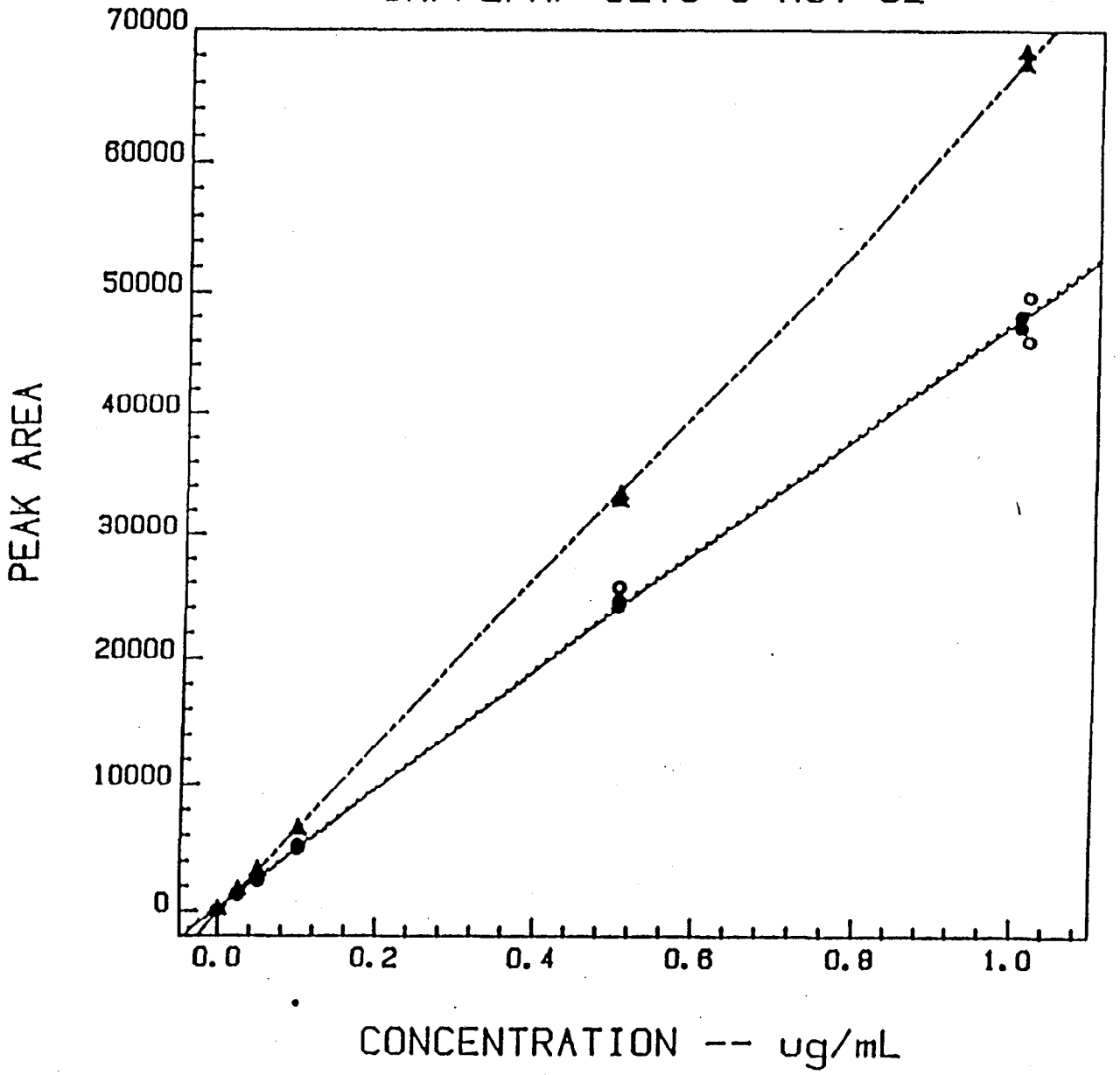
4L/min

15	3.5	2.630	0.410	3.040	13
20	3.5	2.332	0.388	2.720	14
17	1.4	0.916	0.478	1.394	34
19	1.4	0.775	0.553	1.328	42
16	Blank	0.495	ND	0.495	0
18	Blank	0.442	ND	0.442	0

AIHL ND = <0.025 µg/mL or <0.075 µg/sample

MITC STANDARDS CHECK

GR/PL/MF SETS 6 NOV 92



GR STANDARD SET (Gamma)
SYMBOL=▲
LINETYPE= ————————
y=a+b*x
n=12
a=-217.3141 s_a=143.7221
b=67752.7668 s_b=313.2390
$s_{y.x}$=395.1088 r=0.9999

MF STANDARD SET (Mancozeb)
SYMBOL=●
LINETYPE= ————————
y=a+b*x
n=12
a=153.6952 s_a=122.9899
b=47660.1964 s_b=268.0537
$s_{y.x}$=338.1135 r=0.9998

PL STANDARD SET (Paul)
SYMBOL=o
LINETYPE=.....
y=a+b*x
n=12
a=314.2705 s_a=402.1056
b=47780.6028 s_b=869.2349
$s_{y.x}$=1106.1153 r=0.9983

Attachment IV

Table 2. Storage Stability of Methyl Isothiocyanate

Test 1			Test 2			Test 3			Test 4		
µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery
0.50	0.42[a]	84	5.14	4.71[a]	92	21.44	19.8[a]	92	51.45	52.3[a]	102
0.50	0.43[a]	86	5.14	4.93[a]	96	21.44	20.1[a]	94	51.45	53.0[a]	103
0.50	0.43[a]	86	5.14	4.86[a]	95	21.44	19.8[a]	92	51.45	51.1[a]	99
0.50	0.43[a]	86	5.00	4.60[a]	92	21.44	20.4[a]	95	51.45	50.6[a]	98
0.50	0.39[b]	78	5.15	5.16[b]	100	25.47	24.6[b]	97	51.45	50.1[b]	97
0.50	0.39[b]	78	5.15	5.19[b]	101	25.47	24.3[b]	95	51.45	45.3[b]	88
0.50	0.30[c]	76	5.15	4.59[c]	89	25.47	23.2[c]	91	51.45	46.8[c]	91
0.50	0.37[c]	74	5.15	4.71[c]	92	25.47	22.6[c]	89	51.45	55.6[c]	108
0.50	0.38[c]	76	5.14	4.11[c]	80	21.44	15.9[c]	74	51.45	44.9[c]	87
0.50	0.39[c]	78	5.14	4.01c	78	21.44	16.7[c]	78	51.45	45.7c	89

NOTES: a = Samples analyzed after being stored for 1 day under refrigeration
b = Samples analyzed after being stored for 7 days under refrigeration
c = Samples analyzed after being stored for 14 days under refrigeration,
% Recovery not corrected for desorption efficiency (D.E.)

Attachment V

SACRAMENTO AMBIENT MITC BACKGROUND RESULTS

Sample #	Apparent MITC Detected (µg)		Remarks
9	0.163	(0.15)	Sampled for 24 hrs at 1 LPM.
11	0.131	(0.12)	Figures in parentheses are DPR results. GC/MS analyses did not confirm the presence of MITC.
16	0.495		Sampled for 24 hrs at 4 LPM.
18	0.495		GC/MS analyses did not confirm the presence of MITC.
CC-B1	ND*		Sampled for 24 hrs at 1 LPM and 4 LPM in the rain. Water droplets observed in the CS_2 extracts.
CC-B2	ND		
CC-B3	ND		
CC-B4	ND		
CC-B5	ND		Sampled for 24 hrs at 4 LPM.
CC-B6	ND		Samples CC-B5 and CC-B6 were re-analyzed by GC/MS which did not confirm
CC-B7	ND		the presence of MITC.
CC-B8	ND		

*ND = not detected, below the quantitation limit, i.e., < 0.75 µg MITC/sample as determined by GC/NPD analysis

AIHL December 3, 1992